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(12) UK Patent Application (19) GB (11) 2 254 923 (13) A

(43) Date of A publication 21.10.1992

(21) Application No 9207180.2	(51) INT CL ⁶ G01R 33/34, G01V 3/14
(22) Date of filing 01.04.1992	
(30) Priority data (31) 9106789	(32) 02.04.1991 (33) GB
(71) Applicant British Technology Group Limited (Incorporated in the United Kingdom) 101 Newington Causeway, London, SE1 6BU, United Kingdom	(52) UK CL (Edition K) G1N N508 N524 N526 N545 N546 N571 U1S S1310 S1348 S2196
(72) Inventors John Alec Sydney Smith Julian David Shaw	(56) Documents cited GB 2152674 A
(74) Agent and/or Address for Service Paul Dennis Cozens British Technology Group Limited, 101 Newington Causeway, London, SE1 6BU, United Kingdom	(58) Field of search UK CL (Edition K) G1N INT CL ⁶ G01N, G01R, G01V 3/14 3/175 Online databases: WPI, INSPEC

(54) NQR methods and apparatus

(57) The presence within a larger article of a specific substance eg explosives, drugs containing quadrupolar atomic nuclei is detected by performing tests of parts of the article by placing the article adjacent to an array of coils 10, energising with an rf source 20 the coils 10 in periods within a cyclic sequence to irradiate parts of the article with rf pulses of one or more frequencies at or close to a resonant frequency of quadrupolar atomic nuclei within the substance to be detected, connecting the coils 10 in other periods within the cyclic sequence to a phase-sensitive detecting and measuring circuit 15, 24-26 to measure response signals due to nuclear quadrupole resonances, and summing the response signals detected at corresponding instants over a number of cyclic sequences.

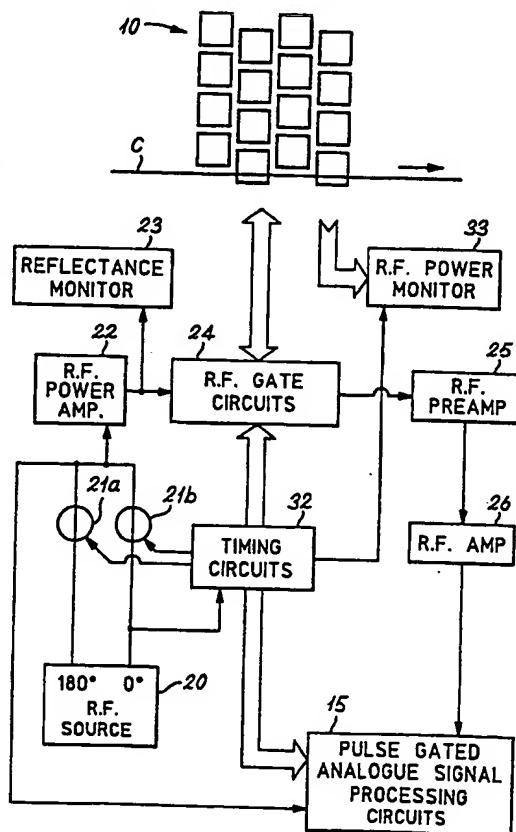


Fig. 2

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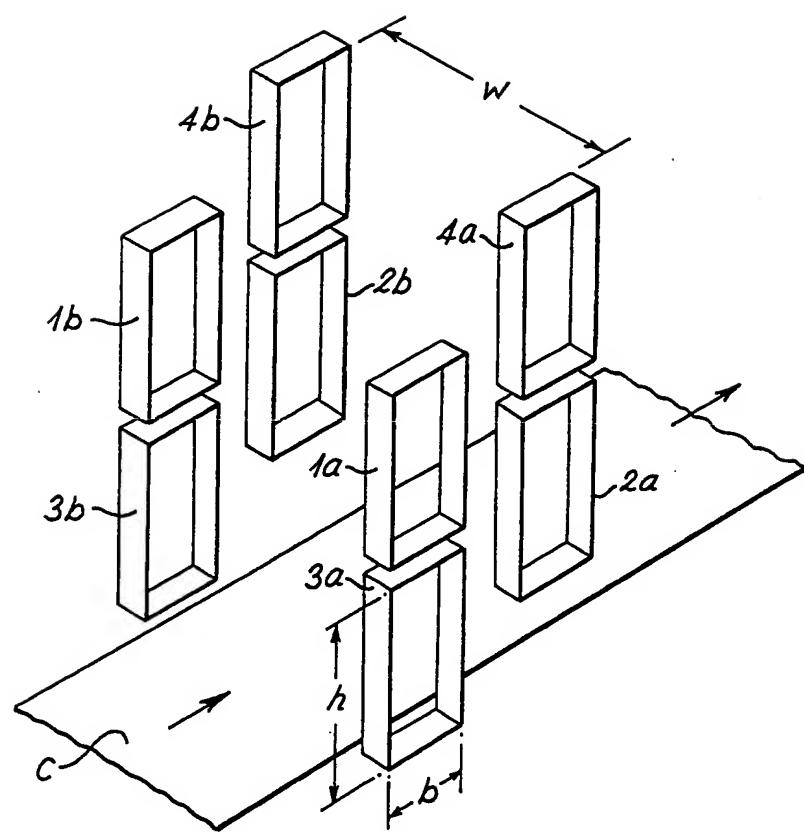


Fig. 1

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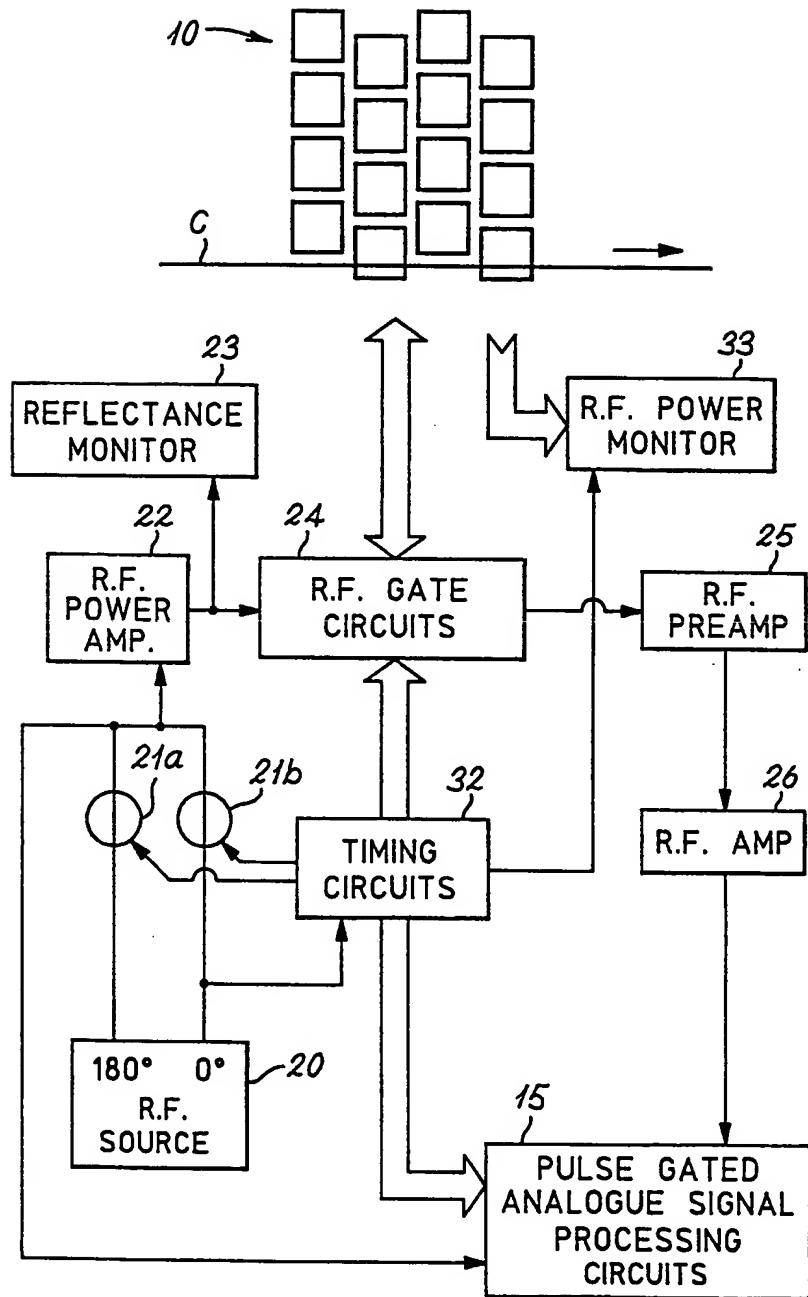


Fig. 2

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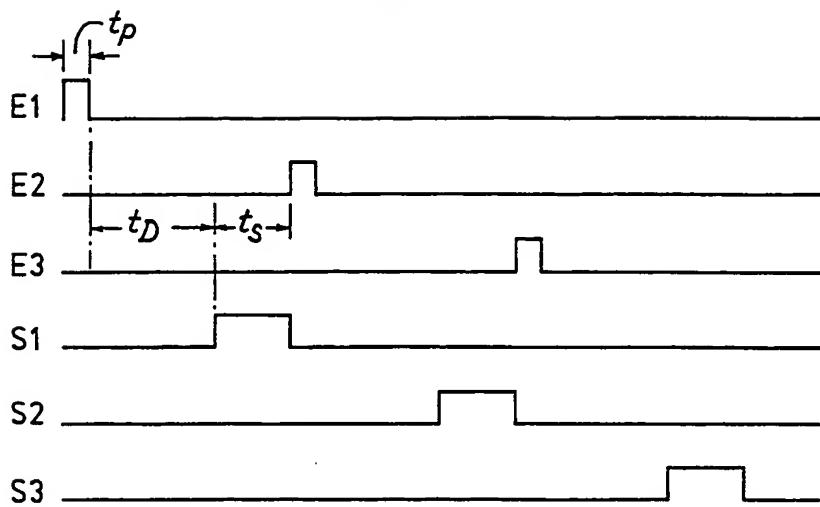


Fig. 3a

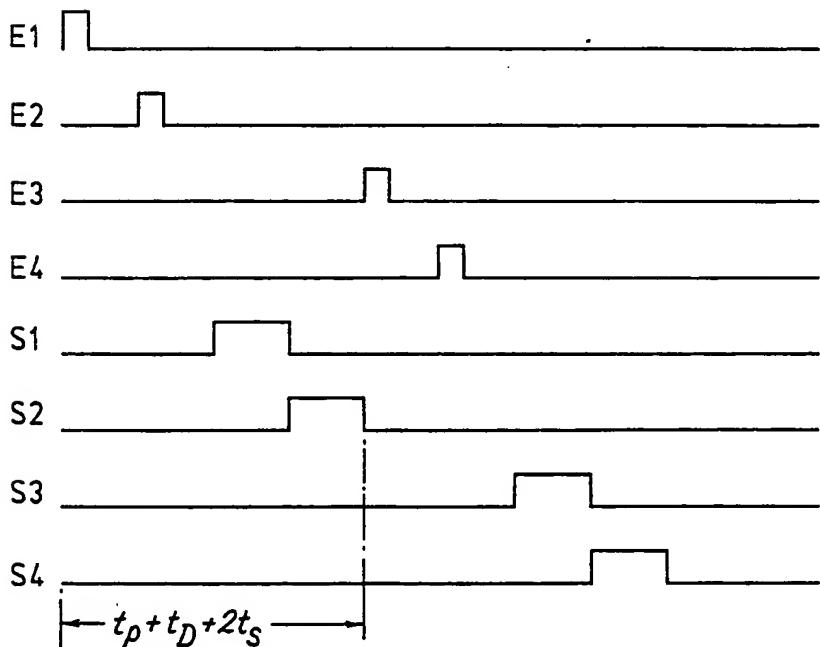


Fig. 3b

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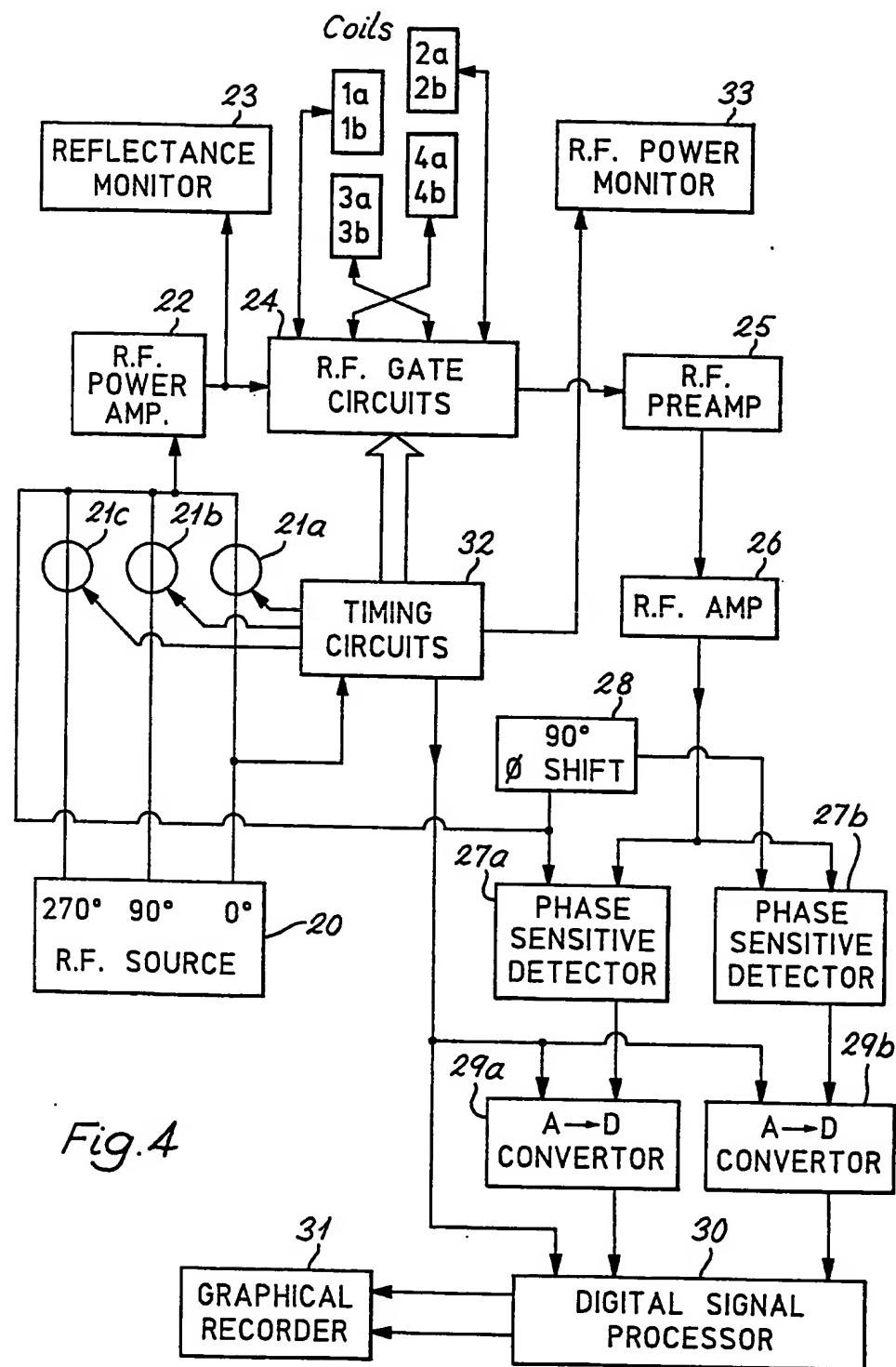


Fig.4

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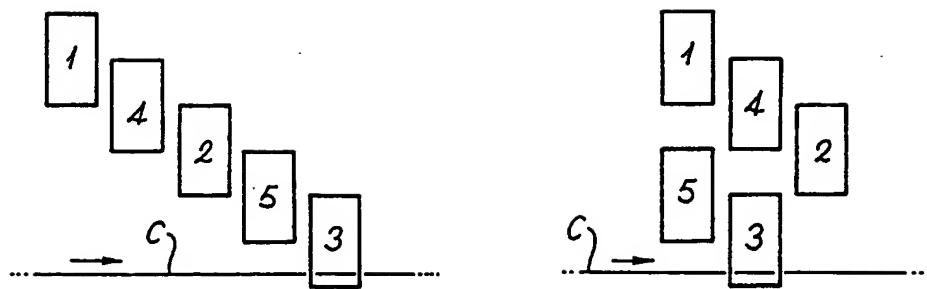


Fig. 5

Fig. 6

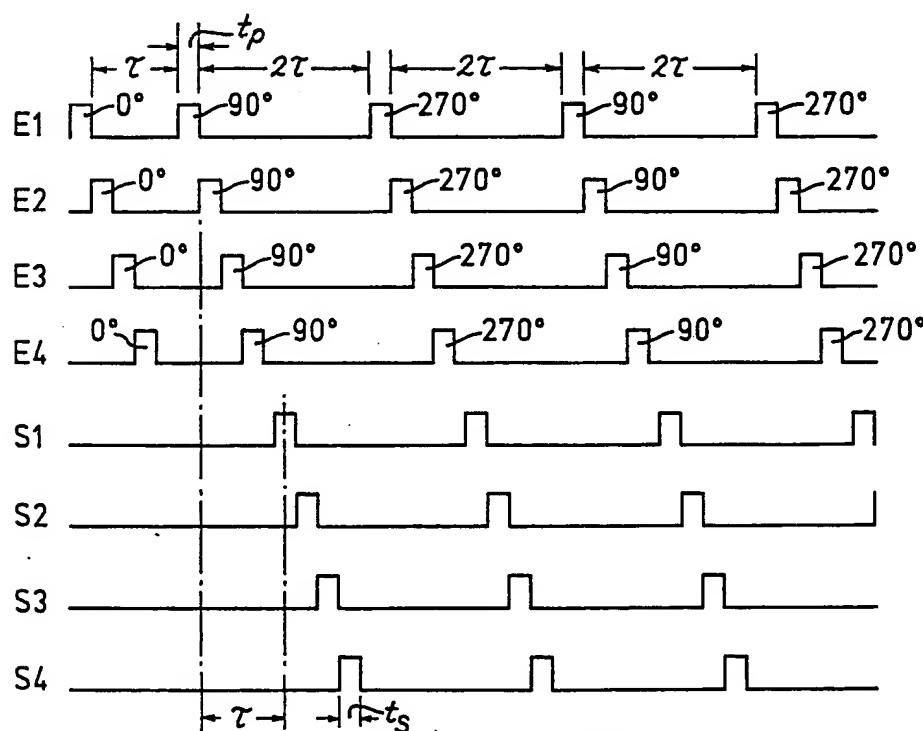


Fig. 7

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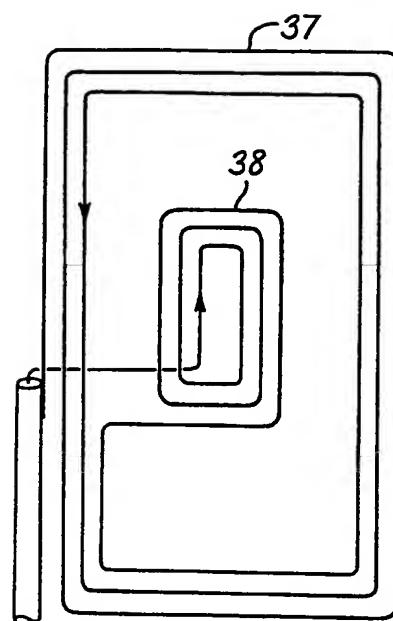


Fig. 8

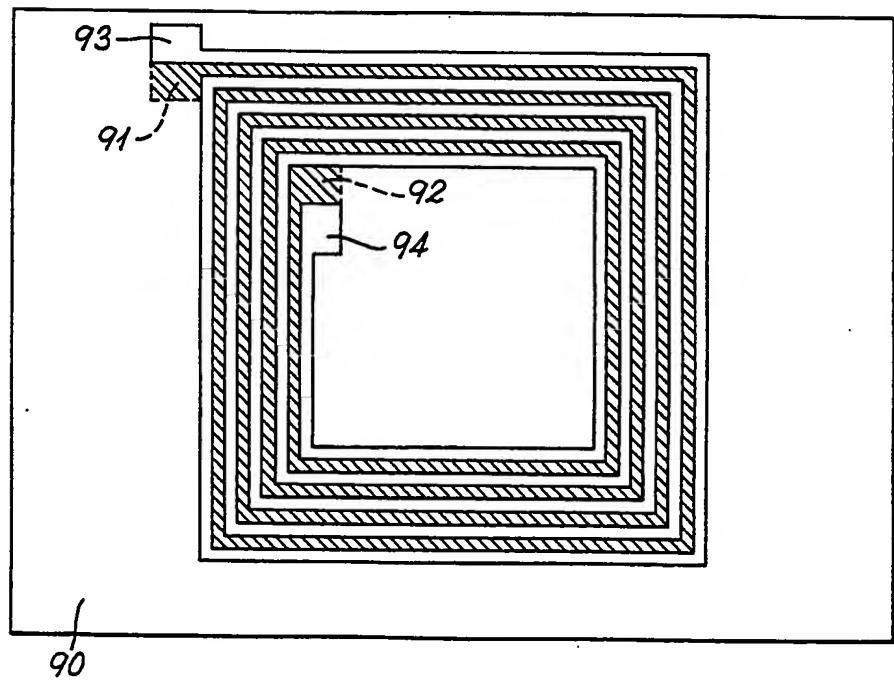


Fig. 9

- 1 -

NQR METHODS AND APPARATUS

This invention relates to methods and apparatus for detecting
the presence of specific substances containing quadrupolar atomic
5 nuclei, in larger articles, by direct observation of nuclear
quadrupole resonance (NQR) effects.

Quadrupolar nuclei have nuclear spin quantum numbers greater
than one half. Common nuclei of this kind include ^7Li , ^9Be , ^{11}B ,
10 ^{14}N , ^{23}Na , ^{27}Al , ^{35}Cl , ^{39}K , ^{55}Mn , ^{59}Co , ^{75}As , ^{79}Br , ^{81}Br , ^{127}I ,
 ^{197}Au , ^{209}Bi and many others - this list should not be
interpreted in any limiting way, it is given simply to note the
potential range of substances which might be detectable by this
technique.

In the sub-molecular environment of compounds or crystals,
15 the nature and disposition of the adjacent electrons and atomic
nuclei produce electric field gradients which modify the energy
levels of any quadrupolar nuclei, and hence give rise to
transition frequencies, to such an extent that measurements of
20 these transition frequencies and/or relaxation time constants can
indicate not merely the nuclei which are present but also their
chemical environment.

NQR measurements have the great advantage that they do not
require the sample to be placed in a strong magnetic field, and
therefore do not require the large, expensive and sample-size
25 limiting magnet structures which are needed for nuclear magnetic
resonance (NMR) measurements. It should be noted that the rules
governing NQR effects are so significantly different from the
rules controlling NMR effects that practices and principles
established in NMR studies do not necessarily apply in NQR work.

30 US Patent 4,887,034 describes methods by which the presence
of various drugs or explosives may be detected indirectly through
the interaction of NQR and NMR effects, but these methods require
a strong magnetic field and the presence of NMR nuclei as well as
35 quadrupolar nuclei in the substances to be detected. The strong
magnetic field would require relatively large magnets with the

added complication that the magnetic field has to be varied between strong and weaker values.

The present invention using direct NQR measurements does not require any background magnetic field or the presence of NMR nuclei.

According to the present invention there is provided a method for detecting the presence within a larger article of a specific substance containing quadrupolar atomic nuclei wherein tests of parts of the article are performed by placing the article adjacent to an array of coils, energising the coils in periods within a cyclic sequence to irradiate parts of the article with radio frequency pulses of one or more frequencies equal or close to a resonant frequency of quadrupolar nuclei within the substance to be detected, connecting the coils in other periods within the cyclic sequence to a phase-sensitive detecting and measuring circuit to measure response signals due to nuclear quadrupole resonance, and summing the response signals detected at corresponding instants over a number of cyclic sequences.

Because only a part of the article has to be irradiated at any given time, the radio frequency drive power required can be greatly reduced over the case where only one coil is provided to irradiate all of the article. At the same time, the sensitivity of detection can be increased due to the fact that smaller volumes of the article are irradiated. Energising the coils in periods within a cyclic sequence can afford the advantage that the test time need be no longer than if only one coil were used. The minimum cycle time is generally limited by the spin-lattice relaxation time, T_1 , of the nuclei. If energisation is supplied to all of the coils within this minimum cycle time, the overall test will take no longer than if only one coil were used, since the arrangement with one coil is still subject to the same cycle time limitation.

Preferably the article is placed between two identical arrays of coils, and corresponding coils in both arrays are simultaneously excited and simultaneously connected to the

detecting and measuring circuit. Alternatively the two arrays can be used in separate tests, and any difference in the results may show that the substance is present towards one side of the article.

5 The method may be repeated with different frequencies appropriate for the detection of different substances. The timing and frequency range or spectrum of the excitation pulses and the timing and duration of the sampling periods may have to be altered for optimum sensitivity in the detection of different
10 substances. It is of particular interest to detect the resonances of ^{14}N nuclei in drugs, for instance heroin or cocaine, or in explosives, for instance HMX, RDX, PETN, or TNT.

The irradiation frequency should be within about 0.1% of the resonant frequency. Environmental conditions such as
15 temperature, pressure or magnetic fields may shift the resonant frequency and it is therefore desirable to modulate or vary the irradiation frequency or alternatively to ensure (e.g. by the use of high-power or composite pulses) that the power spectrum of the irradiation pulses provides substantial power within about 0.1%
20 of any frequency to which the resonance may be shifted by any environmental conditions likely to apply to the articles to be examined. In the examination of airline baggage or airfreight, for instance, it will be desirable to allow for resonant frequency shifts which may be caused by $\pm 20^\circ\text{C}$, preferably $\pm 25^\circ\text{C}$,
25 temperature variations, and in a typical case these shifts may be about $\pm 10\text{kHz}$.

It is also desirable to monitor the loading or matching of the coils to detect the presence of any conducting or ferromagnetic material which could significantly affect the
30 operation of the apparatus or screen the substance from the radio frequency irradiation.

According to the present invention, apparatus for detecting the presence within a larger article of a specific substance containing quadrupolar atomic nuclei comprises an array of coils
35 adjacent to a sample space in which the article can be placed,

excitation means for applying phase-controlled pulses or pulse sequences of radio frequency signals sequentially to the coils so as to irradiate parts of the article with pulses of radio frequency energy having a frequency or a range of frequencies at 5 or close to a resonant frequency of the said nuclei in the substance to be detected, a radio frequency detecting and measuring circuit, switching means for sequentially connecting the coils to the detecting and measuring circuit so that each such connection is made before and is maintained throughout a 10 sampling period at a set time interval after the application of an excitation pulse to the relevant coil, and means for summing signals detected at corresponding instants in the sampling periods of a number of cycles of irradiation and detection.

Preferably the coils of the array are arranged in two or more 15 columns and some means is provided to move, or facilitate the movement of, articles to be examined past the array transversely to the columns. The coils of alternate columns are preferably displaced so that any part of an article which passes adjacent to the sides or abutment of two coils in one column will pass 20 adjacent to the centre of a coil in the next column. Alternatively this effect may be achieved by having coils in a diagonal array.

Preferably the apparatus will have two identical arrays of coils placed on opposite sides of the sample space, and 25 corresponding coils on both sides will be used simultaneously for both excitation and detection. This gives more uniform irradiation and hence more uniform sensitivity.

The apparatus may be made in three sizes - a relatively small size for the examination of letters and small packages, a medium 30 size for the examination of hand luggage and parcels, and a large size for the examination of large suitcases and other baggage. Practically the spacing (w) between the coil arrays will be most important since it will determine the thickest article which can be tested with the normal position of both coil arrays and it 35 will indirectly determine the radio frequency drive power

required. One coil array may be movable or removable, to allow some testing of thicker articles.

To achieve fairly uniform irradiation and hence fairly uniform sensitivity, the corresponding coils of the two arrays 5 may be of the Helmholtz configuration, that is annular coils of radius w separated by the distance w and therefore enclosing and irradiating a volume of πw^3 with a very uniform field strength. If more but smaller coils are used to cover the required height 10 of sample space, the r.f. drive power required will be reduced 10 but the field strength will be less uniform and this will give less uniform sensitivity.

For more efficient coverage of the whole volume of the article, the coils may have turns of a hexagonal or square rather than circular shape. To reduce the required drive power 15 rectangular coils of height h and breadth b may be used, where h is comparable with w and b is smaller than h . For the purpose of detecting articles which contain significant quantities of specific substances, although it is desirable to achieve uniform 20 sensitivity throughout the sample volume, it is not absolutely essential and consequently a less uniform radio frequency field may be used. It has been reported that the use of phase inversion on alternate pulses in some way compensates for effects of a non-uniform radio frequency field strength. Thus h may be reduced to about 0.7 w to give a further saving in the drive 25 power required. The coils may be short solenoids of one or more layers, or may be formed by one or more spiral turns on planar or conical support structures.

A preferred design for a typical coil has two spiral windings 30 of square configuration mounted on respective opposite sides of a planar support and electrically connected in parallel. The spirals may be relatively displaced so that in a side view one spiral winding would appear to lie between the turns of the other, to minimise their self-capacitance.

Material used to support the coils should be a low-loss 35 insulating material which will not show any nuclear quadrupole

resonance which might be confused with or mask the resonance signals from any substance which is to be detected. Each coil will be connected to timing or matching components to minimise r.f. signal reflections.

- 5 Each coil may have some outer turns enclosing a relatively large area and some inner turns enclosing a concentric relatively small area, connected so that the field of the inner turns will oppose the field of the outer turns. This form of coil will use more power for a given strength of irradiation but will provide
10 more uniform irradiation over a greater distance from the face of the coil.

In the simplest form of the invention the cycle time may be made much longer than the spin-lattice relaxation time constant T_1 of the nuclei and the response signals which are measured are
15 parts of the free induction decay (f.i.d.) signals generated immediately after each irradiation pulse. In effect the cycle time may be sufficiently long that the nuclei have time to return to a steady state and the tests are separate and independent. Inevitably the radio frequency pulses applied to the coils will
20 tend to persist as a decaying damped oscillation. This has two consequences; it requires the measuring actions to be delayed until the damped oscillations have sufficiently decayed to avoid overloading the detection circuits, and the residual oscillation signal will be superimposed on the wanted response signals.
25 However, by having the radio-frequency pulses phase-inverted in one-half of the cycles and by using suitable phase-sensitive detector circuits as hereinafter described, the residual oscillations can be made to cancel out substantially. Since the free induction decay signals are also decaying, it is desirable
30 not to delay the measurements any longer than is necessary.

Resonant frequencies appropriate for the detection of different substances may lie anywhere in the range from 50 kHz to 1000 MHz. The optimum physical form of the coils and the maximum Q factor which they may have will depend on the frequency
35 or frequencies to be used. It has been found advantageous to use

coils of the highest available Q factor.

Generally a Q factor of 40 or more will be possible and coils of Q factor = 100 or more have been used in experiments. Such coils will show a decaying r.f. oscillation or ring-down after 5 each excitation pulse, and the higher the Q, the longer this ring-down will persist.

The ring-down signals may be suppressed or reduced by Q-switching arrangements which may use PIN diodes or other controllable switching devices to dissipate the ring-down signal 10 energy quickly after each excitation pulse, thereby allowing the sampling delay t_D to be shortened and higher response signals to be measured. This may be used instead of or in addition to phase-inverting half the irradiation pulses. However, it may be 15 difficult to provide a Q switching arrangement which will be reliable in apparatus using the amount of radio frequency drive power which will be needed for the detection of drugs or explosives hidden in moderately large articles.

However in the simplest form of the invention the total cycle time is not critical. The f.i.d. response signals can be sampled 20 during sampling periods of arbitrary duration and they can be accumulated and measured as analogue signals by a box-car integrating circuit. It may be most convenient to test parts of the article in a simple sequence in which a coil or coil pair is excited by a radio frequency pulse or pulse sequence, there is a 25 set delay time (in which any Q-switching action may be applied) and then the free induction decay response superimposed on the residual decaying oscillation is applied to the phase-sensitive detecting and measuring circuit, this sequence being repeated for the next coil or coil pair and so on until all the coils have 30 been used. The tests may be interleaved in time to some extent, for instance by exciting the second coil or coil pair in the set delay time for the first coil, but it would be impractical to attempt any measurements on one coil while any excitation or any Q switching actions are being applied to any other coil. Hence 35 interleaving will shorten the periods available for sampling and

measuring, and if very short sampling periods are to be used it may be necessary to resort to fast digital sampling and signal processing.

In certain experimental conditions the cycle time or time between pulses applied to the same coil may be made very much shorter than T_1 and substantial free induction decay responses can still be obtained after each of a long succession of pulses. For instance in an experiment with a sample of RDX explosive using a slightly off-resonance excitation frequency of 5.191 MHz and a pair of coils similar to Figure 9 the cycle time was reduced to 2 milliseconds and substantial f.i.d. responses were measured in each of a long succession of cycles.

In another form of the invention the cycle time is reduced to a duration comparable with or shorter than the spin-spin relaxation time T_2 of the quadrupolar nuclei in the substance to be detected, and the response signals which are measured are spin-echo signals consequential on the application of two or more preceding pulses.

The pulses applied to each coil or coil pair must form a series in which the durations, power, intervals, frequencies and relative phases of the radio frequency pulses are controlled so as to produce substantial or optimised spin-echo signals from the substance to be detected if it is present in the article being tested. A preferred form for each series of pulses commences with a pulse of duration t_p and r.f. phase 0° , then an interval τ and then pulses of duration t_p with pulse intervals 2τ , the r.f. phase in these pulses being alternately 90° and 270° . The spin echo responses should occur at a time τ after each of the 90° and 270° pulses. However there are various other pulse sequences, including for example composite sequences with no delays between pulses, which can produce useful results. The r.f. phases used may be optimised experimentally.

The pulse interval 2τ and pulse duration t_p and hence the cycle time must be limited; if they are too long the spin echo responses become smaller very quickly, but when appropriate time

and appropriately off-resonant pulses are used substantial response signals can be measured after each of a long succession of excitation pulses. Because the cycle time is so limited the tests have to be interleaved in time; all the coils or coil
5 pairs are energised in sequence in the first half of each cycle and their responses are sampled and measured in sequence during the second half of the cycle. The periods available for sampling and measuring will be relatively short. It may be possible to use analogue signal measurements but the periods may be so short
10 that fast digital sampling may become necessary or preferable. However the spin-echo responses may often provide a better signal-to-noise ratio than the free induction decay signals. The much shorter cycle time and the interleaving of the tests in this form of the invention will allow a complete examination to be
15 done comparatively quickly.

The duration t_p of each irradiation pulse is preferably optimised. It can be theoretically shown that the optimum pulse duration which maximises the response signals is inversely proportional to the radio frequency field strength. Hence the
20 optimum pulse length can be reduced by increasing the radio frequency drive power, but this must be increased in proportion to the square of the field strength.

To allow for the interleaving of the irradiation and detection sequences and to make the sampling periods coincide
25 with the spin-echo response peaks, if there are n coils in the array then the sampling periods cannot be longer than $\tau/(n-2)$ and the excitation pulse duration should be preferably slightly shorter. It will be convenient to make the excitation pulse length t_p approximately equal to τ/n and to have a short time
30 between the last excitation pulse and the first sampling period.

It will therefore be desirable to make the radio frequency field strength large enough so that this pulse duration τ/n will be equal to, or not much less than, the optimum.

It can be shown theoretically that the response signal
35 strength will vary as the first order Bessel function $J_1(\theta_p)$,

where θ_p is proportional to t_p , which has its first maximum at $\theta_p = 119^\circ$ for $I=1$ and a powdered sample. It follows that if the r.f. field strength is reduced to a value which would make the optimum pulse length equal to $1.5 \tau/n$ but the pulse length 5 actually used is τ/n , the spin-echo responses will be reduced by about 13%, while the r.f. drive power required will be only four-ninths of the drive power needed to optimise the spin echo responses.

The detected signals in each sampling period will include 10 some residual contributions from the damped decaying oscillation or "ring-down" of the excitation signal as well as any resonant emission from the nuclei, but with phase inversion applied to alternate excitation pulses and with a suitable phase-sensitive quadrature detection and measuring system, these residual signals 15 may be cancelled out. To allow for possible stray phase shifts, the 90° and 270° phase shifts may be empirically adjusted for best results.

The invention extends to a method of detecting the presence of selected nuclei in an article, including applying a respective 20 sequence of excitation pulses to the article via each of a plurality of excitation devices to excite the selected nuclei to resonance, the sequences of pulses being interleaved with one another, and detecting the resonances thus excited.

The invention also extends to apparatus for detecting the 25 presence of selected nuclei in an article, comprising a plurality of excitation devices (preferably coils), means for applying a respective sequence of excitation pulses to the article via each of the excitation devices to excite the selected nuclei to resonance, the sequence of pulses being interleaved with one 30 another, and means for detecting the resonances thus excited.

All of the method and apparatus features described above apply to these aspects of the invention, and vice versa.

Embodiments of the invention will now be described, by way of example only, with reference to the accompanying Figures, of 35 which:-

Figure 1 is a perspective sketch showing an arrangement of two coil arrays adjacent to a conveyor belt;

Figure 2 is a block circuit diagram of apparatus as used for measuring f.i.d. responses with a relatively long cycle time;

5 Figures 3a and 3b are graphical diagrams illustrating alternative ways of using the apparatus of Figure 2;

Figure 4 is a block circuit diagram of apparatus as used for measuring spin echo responses with a relatively short cycle time;

10 Figures 5 and 6 are diagrammatic side views of alternative arrangements of coil arrays.

Figure 7 is a graphical representation of signals used in the apparatus of Figures 1 and 4;

Figure 8 is a diagrammatic drawing of a coil with inner and outer turns; and

15 Figure 9 is a side elevation of another useful form of coil.

Figure 1 shows a conveyor belt, represented diagrammatically as a strip C with arrows to show its direction of motion, which is arranged to carry articles (not shown) continuously or intermittently for examination between two arrays of coils. The 20 coils are shown diagrammatically as rectangular frames 1a to 4b of width b and height h. The coils, 1a,3a,2a and 4a are arranged in two columns in a vertical plane above the nearer edge of the conveyor belt C. Coils 1b,3b,2b and 4b are correspondingly arranged in a vertical plane above the further edge of the 25 conveyor belt. The coils 2a,4a,2b,4b are mounted at a height such that any part of an article which passes adjacent to the abutment or edges of the coils 1a,3a,1b,3b will pass between the centres of coils 2a,2b or 4a,4b. The spacing between the arrays of coils is indicated as dimension w.

30 The particular physical design of the coils will depend on the frequency or frequencies to be used, which will depend on the substance or substances to be detected. They are mounted on formers and supports (not shown) of a low loss insulating material which will not show any confusing resonances from any 35 quadrupolar nuclei. To avoid undesirable and illegal stray

radiation the whole apparatus of Figure 1 will be used within a screened room or a tunnel-like enclosure lined with copper or aluminium foil (not shown).

Figure 2 is a block diagram of electrical apparatus suitable for the simpler form of the invention in which f.i.d. signals are measured. At the top of the diagram is a diagrammatic side elevation of the conveyor belt C and an array of coils or coil pairs 10. In this case fourteen coils or coil pairs are shown arranged in four columns but any number of coils may be used in this form of the invention. A radio frequency source 20 has two outputs arranged to provide the same frequency signal with phasing indicated by the annotations 0° and 180°. These outputs are connected through circuits 21a and 21b respectively to a radio frequency power amplifier 22. The amplifier output is connected to a reflectance monitor 23 and through r.f. gate circuits 24 to the coils 10. During the sampling periods the r.f. gate circuits 24 connect the coil pairs through an r.f. pre-amplifier 25 and r.f. amplifier 26 to pulse gated analogue-signal processing circuits 15. Timing circuits 32 are connected to receive a reference signal from the r.f. source 20 and to control the gate circuits 21a,21b, the r.f. gate circuits 24, the analogue-signal processing circuits 15 and an r.f. power monitor 33. This monitor 33 is connected to probes (not shown) adjacent to each of the coils to monitor the irradiation field strengths. The circuits 15 are connected to receive a reference signal from the output connection of gate circuits 21a and 21b.

Figure 3a illustrates one way in which the apparatus of Figure 2 may be used for sequential tests using each coil or coil pair in turn. Traces E1,E2,E3 represent the amplitudes of rectangular excitation pulses applied to the first, second and third coil pairs respectively, and traces S1,S2,S3 respectively represent signals controlling the sampling periods during which the response signals from these coils are measured. Each excitation pulse has a duration t_p and is followed after a delay

t_D by a sampling period t_S . Each test made with a particular coil pair is completed in a time $t_p+t_D+t_S$ and if there are n coil pairs a full cycle of tests is completed in a cycle time given by $n(t_p+t_D+t_S)$. Typical values will be $t_p=40\mu s$, $t_D=200\mu s$, $t_S=120\mu s$ and if $n=14$ the cycle time may be 5.04 milliseconds.

- 5 Figure 3b illustrates an alternative arrangement in which the tests are interleaved. Traces E1 to E4 represent excitation signals applied to the first to fourth coil pairs and traces S1 to S4 represent the corresponding sampling control signals.
- 10 Even-numbered coil pairs are energised in the delay periods following the excitation of the odd-numbered coil pairs, and thus tests with two coils are completed in a time $t_p+t_D+2t_S$. A full cycle is completed in a time $n(t_p+t_D+2t_S)/2$ and with the typical values given this may be 3.36 milliseconds. In some experiments
- 15 the cycle time has been reduced to 2 milliseconds with satisfactory results.

The gates 21a and 21b will be opened in alternate cycles and the analogue-signal processing circuits 15 will be arranged to perform the functions of phase-sensitive detection, ring-down 20 signal cancellation and summation of the response signals from many cycles which will be more fully explained with reference to the circuits of Figure 4.

- Figure 4 shows an arrangement of circuits which may be used to measure spin-echo signals with a relatively short cycle time.
- 25 In this case the r.f. source 20 has three outputs to provide signals with relative phasing as indicated by the annotations $0^\circ, 90^\circ, 270^\circ$ and there are three gate circuits 21a, 21b and 21c which connect these outputs to the r.f. power amplifier. The coil pairs 1a, 1b to 4a, 4b are arranged as shown in Figure 1
- 30 and the number of coil pairs which may be used will be limited by constraints on the cycle time. During the sampling periods the gate circuits 24 will connect the coils to a detecting and measuring circuit which comprises units 25 to 30 inclusive. In the sampling periods signals from the coils 1a to 4b are passed
- 35 through the r.f. gate circuits 24, a low-noise r.f. pre-amplifier

- 25 and an r.f. amplifier 26 to a pair of phase sensitive detector circuits 27a and 27b. The output of the gate circuits 21a, 21b and 21c is connected as a reference signal directly to the p.s.d. circuit 27a and through a 90° phase shifting circuit 28 to the other p.s.d. circuit 27b. Outputs of the p.s.d. circuits 27a and 27b are applied through fast-sampling analogue-to-digital converters 29a and 29b to a digital signal processor unit 30. Outputs from this processor unit 30 are connected to a graphical recorder 31.
- 5 10 Timing circuits 32 receive the reference-phase output of the r.f. source 20 and are arranged to control the gate circuits 21a, 21b, 21c and 24, the fast-sampling converter circuits 29a and 29b, the digital data processor 30 and an r.f. power monitor 33. A number of small r.f. probe pick-up coils, 15 adjacent to each of the coils 1a to 4b but not shown on the diagram for the sake of clarity, are connected to the r.f. power monitor 33, to monitor the actual r.f. field developed by each excitation pulse and thereby show any fault or any malfunction which could be caused by conducting or ferromagnetic material or 20 electrical circuits present within an article which is being tested.
- The coils are generally used in pairs; for example coils 1a and 1b will be energised simultaneously in phase so as to assist in producing a fairly uniform field strength throughout the space 25 between them. However, a switch (not shown) is provided to allow either the array 1a to 4a or the array 1b to 4b to be used separately; such tests will indicate if a detected substance is present towards either side of the article tested.
- 20 30 Figure 7 illustrates a typical sequence of operations for the apparatus of Figure 4 and Figure 1. Traces E₁ to E₄ represent the excitation pulses applied to the coil pairs 1a and 1b, 2a and 2b, 3a and 3b and 4a and 4b respectively. Traces S1 to S4 respectively represent the sampling period control signals for the coil pairs. In the preferred sequence shown there is a 35 preparatory cycle of duration $t+t_p$ without sampling signals, but

in subsequent cycles of duration $2\tau+t_p$ each sequence of coil pair excitations is followed by a sequence of sampling periods and a full set of tests is completed in the time 2τ . Each spin echo response will peak at time τ after the preceding excitation pulse

5 applied to the same coil and the sampling periods are centred on these times. The phase of the radio frequency signals is selected as indicated by the annotations $0^\circ, 90^\circ, 270^\circ$ shown against the pulses. Each coil pair is energised by a series of pulses beginning with a first pulse of reference phase 0° ,

10 followed after a time τ by the first of two sets of excitation pulses. These excitation pulses occur at intervals of 2τ and are alternately of phase 90° and phase 270° ; the 90° phase pulses form one set, and the 270° phase pulses form the other set.

In the preferred arrangement shown the reference signals for

15 the phase sensitive detectors 27a and 27b are taken from the output of the gates 21 and are therefore in phase with the residual ring-down signals. In the digital signal processor 30 the responses measured after the 270° pulses are subtracted from the responses measured after the 90° pulses. This cancels out

20 the ring-down signals but the spin-echo responses are added cumulatively by this procedure. The same effect could be produced by always taking the p.s.d. reference signals directly from one or two of the outputs of the r.f. source 20 and adding all the response signals, but care should be taken to see that

25 stray phase shifts do not detract from the cancellation effect.

To avoid any transients resulting from the connection each sampling period t_s begins shortly after the connection is made. Many samples are taken and digitised in each sampling period.

30 Each test is continued for many cycles, and samples which are digitised at corresponding times in each cycle are summed together. The results stored in the digital data processor therefore comprise four sets of signals each set representing the average or accumulated responses received from one of the coil pairs in a sampling period.

35 For the detection of the explosive RDX a suitable resonant-

frequency is about 5.191 MHz; r.f. drive signals having a power spectrum of width 18 kHz at half height may be used to allow for the effects of $\pm 20^\circ\text{C}$ temperature variations. The r.f. power required for an array as in Figure 1 with $w=25$ cm is

5 about 60 kW. The pulse timing and intervals may be set as follows:-

excitation pulse length $t_p = 40 \mu\text{s}$, peak r.f. field strength approximately 1.1 millitesla (11 gauss), interval $\tau = 175 \mu\text{s}$, cycle time $2\tau = 350 \mu\text{s}$, sampling period $t_s=40\mu\text{s}$, sampling 10 rate 1MHz. Appropriate frequencies for detecting HMX and TNT are 5.303 MHz and 0.875 MHz respectively.

While the traces of Figure 7 show a preferred form of pulse sequence, many other forms of pulse sequence known in NQR or NMR studies can alternatively be used.

15 Figure 8 shows diagrammatically an alternative form of coil which may be used to achieve more uniform irradiation and hence more uniform sensitivity over the thickness of the articles being examined. This has a number of outer turns 37 and a number of inner turns 38, connected so that the field of the inner turns 20 opposes the field of the outer turns. This gives a fairly uniform field extending over a relatively greater distance from the plane of the coil. While the two parts of the coil are drawn as spirals in Figure 3 they could alternatively be short solenoids or annular coils.

25 The sequencing of the coil connections is preferably arranged so that consecutively connected coils are not immediately adjacent to each other, to minimise any cross-coupling which could cause misleading results. This is easier to arrange if the time τ can be longer in relation to the pulse duration t_p so as 30 to allow more than four coils to be used. For instance t_p could be 35 μs and $\tau=200 \mu\text{s}$ for the five-coil arrays of Figures 5 and 6. Alternatively, as indicated in Figures 1 and 2, the second column of coils in each array may be slightly separated from the first column and if necessary an earthed conductive 35 strip (not shown) could be placed between the columns to minimise

cross-coupling.

- Figure 5 shows a side view of an alternative form of array with five coil pairs in a diagonal arrangement. For greater compactness this can be rearranged into the form shown in 5 Figure 6, where the two lowest coil pairs are displaced to positions under the two highest coil pairs. The coil pairs in these arrays can be energised in the sequence indicated by the numbers 1 to 5, so that consecutively connected coils are not adjacent to each other.
- 10 Figure 9 shows a suitable construction for one of the coils. This has two windings, electrically connected in parallel, formed by photo-etching copper coatings on both sides of an insulating board 90. The windings are formed as square spirals; the shaded part extending from 91 to 92 represents the winding on the rear 15 side of the board, and the clear structure from 93 to 94 represents the winding on the front of the board.

It will of course be understood that the present invention has been described purely by way of example, and modifications of detail can be made within the scope of the invention.

CLAIMS

1. A method for detecting the presence within a larger article of a specific substance containing quadrupolar atomic nuclei wherein tests of parts of the article are performed by placing
5 the article adjacent to an array of coils, energising the coils in periods within a cyclic sequence to irradiate parts of the article with radio frequency pulses of one or more frequencies at or close to a resonant frequency of quadrupolar atomic nuclei within the substance to be detected, connecting the coils in
10 other periods within the cyclic sequence to a phase-sensitive detecting and measuring circuit to measure response signals due to nuclear quadrupole resonances, and summing the response signals detected at corresponding instants over a number of cyclic sequences.
- 15 2. A method as claimed in Claim 1, in which the article to be examined is placed between two identical arrays of coils and the method is performed using corresponding coils of both arrays simultaneously.
- 20 3. A method as claimed in Claim 2 in which further tests are made using the coils of each array separately, so that any difference in the results of such tests may show if the substance is present towards either side of the article.
- 25 4. A method as claimed in Claim 1 and wherein a coil is energised with at least one radio frequency pulse and after a set delay time it is connected to a detecting and measuring circuit to measure a free induction decay response induced by the or each pulse, and similar tests are applied to each coil to complete each cyclic sequence.
- 30 5. A method as claimed in Claim 4 and wherein the tests are interleaved in time, by energising another coil or other coils in sequence during the delay time after a coil is energised.
- 35 6. A method as claimed in Claim 1 and wherein the radio frequency phase of the energising pulses is inverted in one half of the pulses and a suitable phase-sensitive detection method is used to cancel out residual ring-down signals.

7. A method as claimed in Claim 1 and wherein the pulses applied to each coil form a series of pulses controlled so as to produce spin-echo signals and the measuring circuit is arranged to measure the spin-echo signals.
- 5 8. A method as claimed in Claim 7 and wherein the pulses applied to each coil form a series commencing with a first pulse of a predetermined reference phase, a first interval of duration τ , and subsequent pulses separated by intervals of duration 2τ (preferably of different phase from the reference phase).
- 10 9. A method as claimed in Claim 8 and wherein the subsequent pulses are in quadrature with the reference phase.
10. A method as claimed in Claim 9 and wherein the subsequent pulses are alternately in phase-advanced and phase-retarded relationship with respect to the reference pulses.
- 15 11. A method as claimed in Claim 8 and wherein in one-half of the cycles used for detection and measurement the phase of the energisation is substantially inverted with respect to the phase of the energisation in the other half of the said cycles.
12. A method as claimed in Claim 1, in which the method is repeated with different radio frequencies selected for detecting specific drugs or explosives.
- 20 13. A method as claimed in Claim 1 in which the loading of the coils is monitored to detect the presence of any electrically conducting or ferromagnetic material which could adversely affect the operation of the apparatus or screen or shield the substance from the radio frequency irradiation.
- 25 14. A method as claimed in Claim 7 and wherein the tests are interleaved in time, the coils being energised consecutively in a set sequence and then connected consecutively to the detecting and measuring circuit in the same sequence during each pulse interval except the first interval of the series.
- 30 15. Apparatus for detecting the presence, in larger articles, of a specific substance containing quadrupolar atomic nuclei, comprising:-
 - 35 an array of coils adjacent to a sample space in which the

article can be placed;

excitation means for applying phase-controlled pulses or pulse sequences of radio frequency signals sequentially to the coils so as to irradiate parts of the article with pulses of

5 radio frequency energy at or close to a resonant frequency of the said nuclei in the substance to be detected;

a radio frequency detecting and measuring circuit; and

switching means for sequentially connecting the coils to the detecting and measuring circuit so that each such connection is
10 made before and is maintained throughout a sampling period at a set time interval after the application of an excitation pulse to the relevant coil;

and means for summing nuclear quadrupole resonance response signals detected at corresponding instants in the sampling
15 periods of a number of cycles of irradiation and detection.

16. Apparatus as claimed in Claim 15, also including means for conveying articles to be examined through the sample space in an intermittent motion or a slow continuous motion, and wherein the coils are arranged in two or more columns transverse to the
20 direction of motion, the coils of alternate columns being displaced so that any part of an article which passes adjacent to the edges or abutment of two coils in one column will pass adjacent to the centre of a coil in the next column.

17. Apparatus as claimed in Claim 15 and also including means for
25 conveying articles to be examined through the sample space in an intermittent motion or a slow continuous motion and wherein the coils are disposed in a diagonal or staggered array to test overlapping parts of each article when it is moved past the coils.

18. Apparatus as claimed in Claim 15 wherein there are two
30 identical arrays of coils on respective opposite sides of the sample space, the excitation means is arranged to apply the radio-frequency signals simultaneously to corresponding coils in both arrays, and the switching means is arranged to connect corresponding coils in both arrays simultaneously to the
35 detecting and measuring circuit.

19. Apparatus as claimed in Claim 15 in which each coil has some outer turns enclosing a relatively large area and some inner turns enclosing a concentric relatively small area, connected so that the field of the inner turns opposes the field of the outer turns.
5
20. Apparatus as claimed in Claim 15 and wherein the frequency or frequency spectrum of the radio frequency signals, the durations and timing of the excitation pulses and the durations and timing of the sampling periods may be set to values appropriate for the detection of specific drugs or explosive substances.
10
21. Apparatus as claimed in Claim 15 and wherein the coils have a Q factor greater than 40.
22. Apparatus as claimed in Claim 15, of a size suitable for the examination of letters and small packages.
- 15 23. Apparatus as claimed in Claim 15, of a size suitable for the examination of larger packages or hand luggage.
24. Apparatus as claimed in Claim 15, of a size suitable for the examination of heavy baggage and large suitcases.
25. Apparatus as claimed in Claim 15 and wherein each coil has
20 two spiral windings mounted on opposite sides of a planar insulating board and electrically connected in parallel.
26. Apparatus as claimed in Claim 25 and wherein the two spiral windings of each coil are relatively placed so that in a side view one spiral winding would appear to lie between the turns of
25 the other spiral winding.
27. A method of detecting the presence of selected nuclei in an article, including applying a respective sequence of excitation pulses to the article via each of a plurality of excitation devices to excite the selected nuclei to resonance, the sequences of pulses being interleaved with one another, and detecting the resonances thus excited.
30
28. Apparatus for detecting the presence of selected nuclei in an article, comprising a plurality of excitation devices (preferably coils), means for applying a respective sequence of excitation pulses to the article via each of the excitation devices to
35

excite the selected nuclei to resonance, the sequences of pulses being interleaved with one another, and means for detecting the resonances thus excited.

29. A method according to any of Claims 1 to 14 wherein the power spectrum of the irradiation pulses provides substantial power within about 0.1% of any frequency to which the resonance may be shifted by any environmental condition likely to apply to the article.
- 10 30. A method according to any of Claims 1 to 14 wherein the irradiation pulses allow for resonant frequency shifts caused by $\pm 20^{\circ}\text{C}$ temperature variations.
31. A method of detecting the presence of selected nuclei in an article substantially as herein described with reference to any of the accompanying drawings.
- 15 32. Apparatus for detecting the presence of selected nuclei in an article substantially as herein described with reference to any of the accompanying drawings.

Examiner's report to the Comptroller under
Section 17 (The Search Report)

Application number

9207180.2

Relevant Technical fields

(i) UK CI (Edition K) G1N (PART G)

Search Examiner

(ii) Int CL (Edition 5) G01N G01R G01V (3/14,3/175)

D C GRACE

Databases (see over)

(i) UK Patent Office

Date of Search

(ii) ONLINE DATABASES: WPI, INSPEC

17 JULY 1992

Documents considered relevant following a search in respect of claims

1-32

Category (see over)	Identity of document and relevant passages	Relevant to claim(s)
X	GB 2152674 A (SOUTHWEST RESEARCH) - eg page 18 line 28 to page 19 line 31	27,28

Category	Identity of document and relevant passages	Relevant to claim(s)
Categories of documents X: Document indicating lack of novelty or of inventive step. Y: Document indicating lack of inventive step if combined with one or more other documents of the same category. A: Document indicating technological background and/or state of the art.		
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